

Supporting information for

Calculation of Chemical-Shift Tensors of Heavy Nuclei:

A DFT/ZORA Investigation of  $^{199}\text{Hg}$  Chemical-Shift Tensors in Solids, and the Effects  
of Cluster Size and Electronic-State Approximations

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**Table S1. Calculated NMR Chemical Shieldings for  
Small and Large Model Clusters of  $^{199}\text{Hg}$  Solids.**

<b>Model clusters</b>	<b><math>\sigma_{11}</math> (ppm)</b>	<b><math>\sigma_{22}</math> (ppm)</b>	<b><math>\sigma_{33}</math> (ppm)</b>
<b>Hg(SCN)<sub>2</sub></b>			
Small Cluster	7505	8998	12511
Large Cluster	7847	8540	11677
<b>Hg(CN)<sub>2</sub></b>			
Small Cluster	7954	7958	13301
Large Cluster	7992	8046	12092
<b>Hg(SeCN)<sub>2</sub></b>			
Small Cluster	8465	9020	12418
Large Cluster	8542	9371	11450
<b>Hg(Acetate)<sub>2</sub></b>			
Small Cluster	9596	9890	12505
Large Cluster	9975	10102	11653
<b>HgF<sub>2</sub></b>			
Small Cluster	11578	11578	11578
Large Cluster	10887	10888	10888
<b>HgCl<sub>2</sub></b>			
Small Cluster	7987	7987	13181
Large Cluster	8284	8340	12319
<b>HgBr<sub>2</sub></b>			
Small Cluster	9964	9965	13142
Large Cluster	9926	9957	11398
<b>HgI<sub>2</sub></b>			
Small Cluster	11444	12293	12348
Large Cluster	10710	10750	11296
<b>Hg<sub>2</sub>Cl<sub>2</sub></b>			
Small Cluster <u>Hg(1)</u>	7683	7683	13203
Small Cluster <u>Hg(2)</u>	7683	7683	13203
Large Cluster <u>Hg(1)</u>	8031	8031	11612
Large Cluster <u>Hg(2)</u>	8002	8002	11612

<b>K[Hg(SCN)<sub>3</sub>]</b>			
Small Cluster	8021	8557	10208
Large Cluster	7883	8243	9837
<b>Hg<sub>2</sub>(H<sub>2</sub>O)·2NO<sub>3</sub></b>			
Small Cluster <u>Hg(1)</u>	9455	9516	13027
Small Cluster <u>Hg(2)</u>	9392	9497	13027
Large Cluster <u>Hg(1)</u>	9024	9113	12069
Large Cluster <u>Hg(2)</u>	8849	9126	12066

**Table S2. Frozen Inner Shells in FCA(TZP)/AE and FCA(DZ)/AE Basis Sets for the Elements in Large Clusters.**

<b>Elements</b>	<b>Frozen Core Orbitals*</b>
Hg	[...]4f
S, Cl	[...]2p
C, N, O, F	[...]1s
Se, Br	[...]3p
I	[...]4p

\*Frozen inner shells are up to and including the listed orbitals for the given elements.

**Table S3. Calculated NMR Chemical Shieldings of Large Clusters with FCA/TZP and FCA/DZ level of basis sets.**

<b>Model clusters</b>	<b><math>\sigma_{11}</math> (ppm)</b>	<b><math>\sigma_{22}</math> (ppm)</b>	<b><math>\sigma_{33}</math> (ppm)</b>
<b>Hg(SCN)<sub>2</sub></b>			
FCA(TZP)/AE	7860	8554	11670
FCA(DZ)/AE	7880	8640	11646
<b>Hg(CN)<sub>2</sub></b>			
FCA(TZP)/AE	8003	8044	12102
FCA(DZ)/AE	8058	8100	12127
<b>Hg(SeCN)<sub>2</sub></b>			
FCA(TZP)/AE	8535	9377	11464
FCA(DZ)/AE	8599	9333	11574
<b>Hg(Acetate)<sub>2</sub></b>			
FCA(TZP)/AE	9975	10100	11656
FCA(DZ)/AE	9980	10101	11749
<b>HgF<sub>2</sub></b>			
FCA(TZP)/AE	10831	10832	10832
FCA(DZ)/AE	10901	10902	10902
<b>HgCl<sub>2</sub></b>			
FCA(TZP)/AE	8286	8362	12326
FCA(DZ)/AE	8334	8400	12355
<b>HgBr<sub>2</sub></b>			
FCA(TZP)/AE	9935	9962	11353
FCA(DZ)/AE	9939	9967	11455
<b>HgI<sub>2</sub></b>			
FCA(TZP)/AE	10709	10753	11197
FCA(DZ)/AE	10637	10677	11088
<b>Hg<sub>2</sub>Cl<sub>2</sub></b>			
FCA(TZP)/AE <u>Hg(1)</u>	8058	8058	11609
FCA(TZP)/AE <u>Hg(2)</u>	8028	8028	11609
FCA(DZ)/AE <u>Hg(1)</u>	8108	8108	11744
FCA(DZ)/AE <u>Hg(2)</u>	8092	8092	11744
<b>K[Hg(SCN)<sub>3</sub>]</b>			
FCA(TZP)/AE	7893	8263	9848
FCA(DZ)/AE	7875	8306	9845
<b>Hg<sub>2</sub>(H<sub>2</sub>O)·2NO<sub>3</sub></b>			
FCA(TZP)/AE <u>Hg(1)</u>	9041	9116	12093
FCA(TZP)/AE <u>Hg(2)</u>	8869	9137	12089
FCA(DZ)/AE <u>Hg(1)</u>	9069	9093	12101
FCA(DZ)/AE <u>Hg(2)</u>	8901	9163	12102

**Table S4. Calculated NMR Chemical Shieldings of Large Clusters with ZORA/Scalar and Nonrelativistic level of theory.**

<b>Model clusters</b>	<b><math>\sigma_{11}</math> (ppm)</b>	<b><math>\sigma_{22}</math> (ppm)</b>	<b><math>\sigma_{33}</math> (ppm)</b>
<b>Hg(SCN)<sub>2</sub></b>			
ZORA/Scalar	6162	6172	8607
Nonrelativistic	6366	6535	8702
<b>Hg(CN)<sub>2</sub></b>			
ZORA/Scalar	5643	5666	8914
Nonrelativistic	6190	6221	8971
<b>Hg(SeCN)<sub>2</sub></b>			
ZORA/Scalar	6049	6224	8507
Nonrelativistic	6115	6455	8707
<b>Hg(Acetate)<sub>2</sub></b>			
ZORA/Scalar	6723	6959	8741
Nonrelativistic	7366	7439	8880
<b>HgF<sub>2</sub></b>			
ZORA/Scalar	7821	7821	7822
Nonrelativistic	8158	8159	8159
<b>HgCl<sub>2</sub></b>			
ZORA/Scalar	6499	6500	8676
Nonrelativistic	6593	6593	8820
<b>HgBr<sub>2</sub></b>			
ZORA/Scalar	6356	6358	8380
Nonrelativistic	6411	6413	8563
<b>HgI<sub>2</sub></b>			
ZORA/Scalar	5810	5814	5863
Nonrelativistic	6298	6300	6378
<b>Hg<sub>2</sub>Cl<sub>2</sub></b>			
ZORA/Scalar <u>Hg(1)</u>	6499	6500	8676
ZORA/Scalar <u>Hg(2)</u>	6496	6497	8676
Nonrelativistic <u>Hg(1)</u>	6593	6593	8820
Nonrelativistic <u>Hg(2)</u>	6593	6593	8821
<b>K[Hg(SCN)<sub>3</sub>]</b>			
FCA/TZP	5687	5781	7047
FCA/DZ	6088	6276	7454
<b>Hg<sub>2</sub>(H<sub>2</sub>O)·2NO<sub>3</sub></b>			
ZORA/Scalar <u>Hg(1)</u>	7151	7165	9061
ZORA/Scalar <u>Hg(2)</u>	7086	7181	9063
Nonrelativistic <u>Hg(1)</u>	7028	7145	9084
Nonrelativistic <u>Hg(2)</u>	7027	7145	9083